ENERGY STORAGE DEVICES HAVING ANODES CONTAINING MG AND ELECTROLYTES UTILIZED THEREIN

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with Government support under Contract DE-AC0576RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND

Low-cost and high-safety battery technologies are critical for both transportation and grid energy storage applications. Significant efforts have been made in the past years to move the energy storage beyond lithium-ion battery technology. Magnesium batteries are one promising technology because of the high volumetric capacity (3832 mAh/cm^3 for Mg metal, in comparison 2062 mAh/cm^3 for Li metal and 1136 mAh/cm^3 for Na metal), improved safety (nondendritic and less chemically active compared to Na and Li metal), and potentially low cost given the natural abundance of Mg.

Traditional electrolytes for Mg batteries made by mixing conventional Mg salts (e.g., $Mg(ClO_4)_2$) and traditional solvents (e.g., propylene carbonate) do not typically support reversible plating/stripping of Mg. This is usually attributed to the formation of a solid electrolyte interphase (SEI) layer that does not conduct Mg^{2+} due to the two valence nature of Mg^{2+}. Reversible Mg plating/stripping has been observed with some electrolyte compositions, almost all of them in-situ synthesized. However, most of these electrolytes contain highly volatile solvents, such as THF. Furthermore, none of the traditional electrolytes exhibit a sufficiently high cycling stability as measured by the coulombic efficiency—or the capacity fade. Therefore, a need exists for Mg energy storage devices and electrolytes for such devices that exhibit high cycling stability (i.e., little or no capacity fade for Mg plating/stripping).

SUMMARY

This document describes energy storage devices having anodes comprising magnesium as well as electrolytes for such energy storage devices. Capacity fade at the anode can exhibit significantly improved performance in the embodiments described herein compared to current state of the art devices.

In one embodiment, an energy storage device has an anode comprising Mg and an electrolyte solution. The electrolyte solution comprises an organic solvent comprising diglyme, triglyme, tetraglyme, or a combination thereof. A first salt comprising a magnesium cation is substantially dissolved in the organic solvent. The solution further comprises a second salt that enhances the solubility of the first salt and comprises magnesium cation or a lithium cation. The first salt, the second salt, or both comprises a BH_4 anion.

As used herein, glyme, diglyme, triglyme, and tetraglyme can refer to dimethoxyethane (DME), diglycol methyl ether, triethylene glycol dimethyl ether, and tetrathylene glycol dimethyl ether, respectively. The term glymes can refer to any of DME, diglyme, triglyme, tetraglyme, or a combination thereof.

In some embodiments, the first salt can comprise $Mg(TFSI)_2$. In others, the first salt comprises $Mg(BH_4)_2$. For embodiments in which the first salt comprises the BH_4 anion, the second salt can comprise a Bis(Trifluoromethanesulfonyl)Imide (TFSI) anion. Alternatively, the second salt can comprise a PF_6 anion.

In preferred embodiments, the device is a rechargeable energy storage device and reversibly plates and strips Mg. The cycling stability of the device can be quantified by the Coulombic efficiency or the capacity fade within a certain number of cycles. In some instances, the anode has a capacity fade less than 80% within 50 cycles. In other instances, the anode has a capacity fade less than 10% within 50 cycles. Preferably, the anode has a capacity fade less than 10% within 100 cycles. Most preferably, the anode has no obvious capacity fade within 100 cycles.

Another embodiment encompasses a rechargeable energy storage device reversibly plating and stripping Mg. The device has an anode capacity fade less than 10% within 100 cycles and comprises a magnesium-containing anode and an electrolyte solution. The electrolyte solution comprises an organic solvent selected from the group consisting of diglyme, triglyme, tetraglyme, and combinations thereof. The solution further comprises a first dissolved salt comprising $Mg(BH_4)_2$ and a second dissolved salt selected from the group consisting of $LiBH_4$, LiTFSI, $LiPF_6$, $Mg(TFSI)_2$, $Mg(PF_6)_2$, and combinations thereof.

In yet another embodiment, an electrolyte solution for energy storage devices having an anode comprising magnesium comprises an organic solvent, a first salt, and a second salt. The organic solvent comprises diglyme, triglyme, tetraglyme, or combinations thereof. The first salt comprises a magnesium cation and the second salt, which enhances the solubility of the first salt, comprises a magnesium cation or a lithium cation. The first salt, the second salt, or both comprise a BH_4 anion.

The purpose of the foregoing summary is to enable the United States Patent and Trademark Office and the public generally, especially the scientists, engineers, and practitioners in the art who are not familiar with patent or legal terms or phraseology, to determine quickly from a cursory inspection the nature and essence of the technical disclosure of the application. The summary is neither intended to define the invention of the application, which is measured by the claims, nor is it intended to be limiting as to the scope of the invention in any way.

Various advantages and novel features of the present invention are described herein and will become further readily apparent to those skilled in this art from the following detailed description. In the preceding and following descriptions, the various embodiments, including the preferred embodiments, have been shown and described. Included herein is a description of the best mode contemplated for carrying out the invention. As will be realized, the invention is capable of modification in various respects without departing from the invention. Accordingly, the drawings and description of the preferred embodiments set forth hereafter are to be regarded as illustrative in nature, and not as restrictive.

DESCRIPTION OF DRAWINGS

Embodiments of the invention are described below with reference to the following accompanying drawings.

FIG. **1**A includes cyclic voltammograms on Pt electrodes in saturated $Mg(BH_4)_2$/diglyme with $LiBH_4$ of various concentrations (20 mV/s).

FIG. **1**B includes the coulombic efficiency and current density for Mg plating/stripping (data obtained from FIG. **1**A).